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EFFECT OF METAL OXIDES ON THE MICROSTRUCTURE OF ZINC CERAMIC

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The effect of crystallization of ZnO on volt-ampere characteristics was investigated. It was shown that incorporation of Bi_2O_3, TiO_2, and SnO_2 causes crystal growth, while Sb_2O_5, CoO, and MnO slow crystal growth. The formation of a finely crystalline structure with thin layers of glass phase increases the volt-ampere characteristics.

The evolution of electrical engineering and electronics is linked with the extensive use of nonlinear elements in instruments and devices where a functional nonlinear dependence is a performance characteristic. Many technical problems can be solved with such elements, which have a nonlinear volt-ampere characteristic (VAC): regulating and stabilizing operation of individual blocks of electronics equipment, improving the interference-killing feature of automatic amplification regulation systems.

Varistors — semiconducting resistors with a nonlinear volt-ampere dependence — are such elements. Varistors have high electric resistance at low voltage (similar to dielectrics) but low resistance (high conductivity) at high voltage (similar to conductors). The electrical properties of these devices cannot be described by Ohm's law and for this reason they are called "non-ohmic."

The first varistors were made from silicon carbide by the usual methods in ceramics technology. Due to the many drawbacks of SiC varistors (low nonlinearity, low level of protection), zinc oxide varistors are now used.

The electrical characteristics of such varistors are determined by the states of the layer on the zinc oxide grain boundary. They have a nonlinear current:voltage ratio, where a 5% change in the voltage is sufficient to increase the current by one order of magnitude and more.

The varistors are formed during sintering of the ceramic, so that a structure consisting of semiconducting ZnO grains surrounded by an insulating layer is formed. These layers are formed on the grain boundaries by adding the oxides of such elements as Bi, Co, Si, Sb, Mn, etc.

Zinc oxide, which serves as the semiconducting phase ($\rho_v \leq 1\ \Omega \cdot cm$) at room temperature, is the basic component of the varistor. In addition to ZnO, the ceramic contains a small amount of other metal-oxide constituents (called a "metal-oxide varistor"). A typical varistor composition is (molar content, %) [1]: 97 ZnO, 1 Sb_2O_3, 0.5 Bi_2O_3, CoO, MnO, and Cr_2O_3.

The varistor consists of ZnO grains of size d surrounded by a thin layer (several nanometers) [2, 3] enriched with cations of the additives (Fig. 1). The typical grain size is approximately 10 μm, and individual resistance of the grains is a maximum of $1\ \Omega \cdot cm$. An insulating boundary layer approximately 100 nm thick is formed on the boundary of each grain. These layers control operation of the varistor.

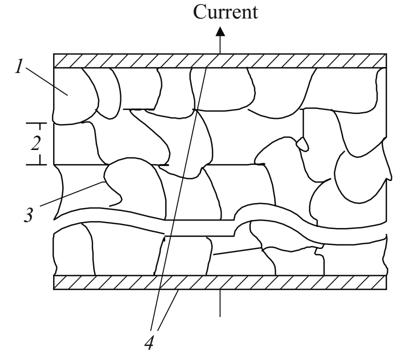

Fig. 1. Microstructure of a varistor ceramic: *1*) grain; *2*) grain of size d; *3*) grain boundary; *4*) electrodes.

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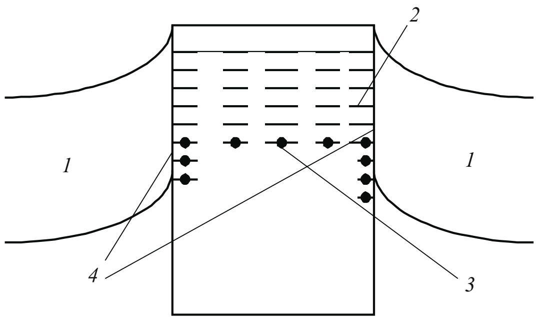

Fig. 2. Structure of the intergranular layer: *1*) ZnO grain; *2*) empty levels; *3*) traps; *4*) surface of intergranular layer.

The electrical properties of the varistors are only determined by the behavior of the individual grain – grain boundaries and the voltage of the varistor is a function of the number of grain boundaries between the electrodes. However, homogeneity of the microstructure is also an important characteristic of the device, since the conductivity between electrodes occurs along a multitude of parallel paths. The ZnO crystal is a semiconductor with a forbidden band width of 0.5 eV, but sintered ZnO has marked conductivity. This conductivity arises due to low donor levels in ZnO due to oxygen vacancies created during sintering at approximately 1200°C [3]. The specific resistance of the grains can be controlled to some degree with such additives as aluminum and lithium oxide.

The mechanism of conductivity for the non-ohmic ZnO ceramic can be useful for explaining the experimental results. The non-ohmic properties of the ZnO ceramic are due to the presence of intergranular layers with high resistance between grains of ZnO with low resistance. The structure consists of an intergranular layer surrounded from both sides by Schottky barriers (Schottky defects) formed on the surface of the ZnO grains (*n*-type semiconductor), as shown in Fig. 2. The thickness of the intergranular layer is a maximum of 50 nm and it has many traps (defects). Schottky barriers arise due to surface states caused by incorporation of dopants that strongly affect the nonlinear properties of the ZnO ceramic.

Hypotheses were advanced in [4, 5] concerning the existence of an intergranular phase from 100 to 500 Å thick surrounding the grains of zinc oxide. However, in later studies [6] using high-resolution electron microscopic methods, it was shown that most intergranular boundaries contain no separate phase. No discrete phase was also found on intergranular boundaries as a result of studies of industrial varistor materials by thin-film x-ray spectrometry and Auger spectrometry [7], but it was found that the regions of the intergranular boundaries are enriched with bismuth in a zone 20 – 100 Å thick on both sides of the boundary. All of this and the well-known concept that ions of large radius such as bismuth, barium, or praseodymium ions must be present to ensure nonlinearity of VAC forms the basis for suggesting that the presence of these impurities in a narrow region adjacent to the intergranular boundary significant affects the varistor effect.

Electrons entering the intergranular layer from the conduction band of ZnO grains by thermionic emission over a direct Schottky barrier move inside it by multituneling along traps or as a limited space charge current and attain surface states on the opposite side of the layer. Then they tunnel through the reverse Schottky barrier of surface states to the conduction band according to the mechanism of field emission at voltage *U* higher than the breakdown voltage and thermionic emissions at *U* lower than the breakdown *U*. The volt-ampere dependences of ZnO ceramic are basically controlled by the reverse Schottky barrier so that the temperature dependence of the mechanisms in the direct Schottky barrier, in the intergranular layer, as well as its thickness, insignificantly affect the character of the curves.

Pure oxides are used as dopants in the zinc oxide ceramic varistor: Bi_2O_3, Sb_2O_3, CoO, MnO, and others. High requirements are imposed on the initial materials, both with respect to purity and dispersion composition to obtain a homogeneous microstructure of the sintered body. The dopants added to ZnO affect formation of the microstructure and consequently the electrical and performance properties of the varistors differently.

Dopants are divided into three basic groups according to the functional application:

those participating in formation of the basic microstructure of ZnO varistors; in sintering, they provide for formation of intergranular layers; Bi_2O_3 is one such dopant;

those used to ensure nonlinearity of the varistor ceramic; they promote the creation of deep charge carrier traps and are the cause of formation of the surface potential of the grains; CoO and MnO are such dopants;

those that stabilize intergranular layers under electric loads and external environmental factors (temperature and humidity) and increase the stability of the electrical characteristics and reliability of the varistors; Sb_2O_3 is one such dopant.

ZnO varistors doped with small amounts of Bi_2O_3 or Pr_2O_3 have been widely used to protect electronic systems from transient overvoltages [8, 9].

The electrical barriers on the grain boundaries arise in sintering of ZnO with dopants and subsequent growth of grains and it is believed that they are responsible for the great nonlinearity of the devices. The VAC of these varistors is a function of the concentration and dispersion of the dopants and the size of the ZnO grains [10]. Large ZnO grains cause low voltage in the varistors and small ZnO grains cause high voltage. The ZnO grains are subject to significant growth during heat treatment in the presence of Bi_2O_3 or Pr_2O_3; their growth can be regulated by addition of K_2O [11].

Co_3O_4 dopant has the greatest effect on the specific electric resistance. Excluding this dopant from the ceramic increases the specific resistance of the crystals. The distribution of elements in a ZnO varistor doped with praseodymium, cobalt, calcium, chromium, and potassium ions was

investigated with Auger electron spectroscopy. It was found that praseodymium, potassium, and calcium ions are segregated in the region of the grain boundaries. No peak corresponding to the cobalt ion was observed, which indicates that the cobalt ion is uniformly dissolved in the ZnO grains. When the dopant content changed, a change was observed in the concentration of oxygen ions in the Auger electron spectra.

When the content of V_2O_5 increases, the size of the ZnO crystals decreases and their specific resistance increases, which can be attributed to an increase in the thickness of the intercrystallite layer whose contribution to the VAC of the ceramic cannot be neglected. This is indirectly confirmed by the decrease in the nonlinearity coefficient of the VAC with an increase in the V_2O_5 dopant content.

Low-voltage ZnO varistors doped with TiO_2 were manufactured with breakdown voltage of 8 – 10 V/mm. The low value of the breakdown voltage is due to the inhomogeneity of the structure, which contains large individual grains. A comparison of the distribution by voltage and the distribution by grain size shows that not all grain boundaries are electrically active. The inhomogeneous microstructure is probably due to the combined effect exercised by TiO_2 dopant and the limited amount of liquid phase. During sintering, titanium ions are rapidly distributed in the liquid phase and increase the chemical activity with respect to the ZnO particles and thus accelerate enlargement of the microstructure [12].

The studies showed that there is an intergranular layer consisting of Pr_2O_3, which significantly affects the properties of the grain boundaries of varistors, in the region of the grain boundaries in ZnO varistors with Pr_6O_{11} dopant. It was found that Pr_2O_3 crystals are formed as a result of oxidation of intergranular $ZnPr_6O_{11}$ atoms.

The grain size and characteristics of the layers (barriers) can thus be controlled by incorporation of different dopants.

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